

Systematics of small parahydrogen clusters in two dimensions

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We studied by means of computer simulations the low temperature properties of two-dimensional parahydrogen clusters comprising between $N = 7$ and 30 molecules. Computed energetics is in quantitative agreement with that reported in the only previous study [Phys. Rev. B **65**, 174527 (2002)], but a generally stronger superfluid response is obtained here for clusters with more than ten molecules. Moreover, all the clusters, including the smallest one, display a well-defined, clearly identifiable solidlike structure; with only one exception, those with fewer than $N = 25$ molecules are superfluid at the lowest temperature considered here (i.e., $T=0.25$ K), and can thus be regarded as nanoscale “supersolids”. The implications of these results on a possible bulk two-dimensional superfluid phase of parahydrogen are discussed.

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I. INTRODUCTION

The physics of small parahydrogen clusters is of interest because these few-body systems feature a rather unique interplay of classical and quantum physics.¹ Due to its low mass and bosonic character, parahydrogen ($p\text{-H}_2$) was predicted a long time ago to undergo a superfluid transition, at temperature $T \lesssim 6$ K.² However, the equilibrium phase of bulk $p\text{-H}_2$ in the $T \rightarrow 0$ limit is a crystal, even in reduced dimensions,^{3,4} due to the depth of the attractive well of the interaction potential between two hydrogen molecules. The theoretical suggestion that a liquidlike phase of $p\text{-H}_2$ could be stabilized in two dimensions (2D) by an underlying impurity substrate⁵ is not supported by several recent calculations.^{6,7}

There is experimental evidence, on the other hand, that small clusters of $p\text{-H}_2$ in three dimensions can escape crystallization,⁸ down to a temperature sufficiently low that a finite superfluid response, defined as the dissipationless rotation about an axis going through the center of mass, arises in the smallest droplets ($\lesssim 30$ molecules) at a temperature of the order of a few tenths of a K.^{9–11} Most of these clusters are expected to remain essentially liquidlike, i.e., structureless, all the way to zero temperature, in some cases undergoing quantum melting at sufficiently low T ; one of them, however, namely $(p\text{-H}_2)_{26}$, is predicted to retain some well-defined structural short-range order, even with the concurrent development of superfluid coherence at low T , behaving in some sense as a finite-size “supersolid”.¹²

An interesting question is what happens if clusters are themselves confined to 2D, which could be experimentally achieved for example by adsorbing a low-density $p\text{-H}_2$ film on a suitable substrate, strong enough to confine molecules effectively to 2D, but also weak enough to allow for the neglect of corrugation. Substrates of alkali metals might be a good candidate,¹³ but progress toward the stabilization of quasi-2D H_2 clusters on a different type

of substrate has been recently reported.¹⁴ Reduction of dimensionality brings about two competing effects. On the one hand, the lower coordination number is expected to weaken the tendency of the system to crystallize, but also has the effect of rendering less frequent quantum-mechanical exchanges of identical particles, which have been shown to play a crucial role in the stabilization of a liquidlike structure at low T .^{10,11}

The only existing theoretical study of $p\text{-H}_2$ clusters in 2D is that by Gordillo and Ceperley, who carried out first principles Path Integral Monte Carlo simulations, down to $T = 0.3$ K.¹⁵ Their main physical findings were that clusters comprising at the most two concentric shells of molecules around the center of mass (typically ten molecules or less) are essentially structureless, i.e., liquidlike, and superfluid at low T ($\lesssim 1$ K); as more molecules are added to the cluster, a solidlike core starts forming, with the concomitant, gradual suppression of the superfluid response. From this observation, the authors inferred that, as cluster size is increased, superfluidity is progressively confined to a liquidlike outer shell, while the solidlike core is insulating.

In this paper, we present results of Quantum Monte Carlo simulations of 2D $p\text{-H}_2$ clusters of size ranging from $N = 7$ to $N = 30$ molecules at low temperature (down to 0.25 K). We computed energetic and superfluid properties of the clusters, and investigated their structure by means of density profiles computed with respect to the center of mass of the cluster, as well as through actual density maps, affording direct visual insight in 2D.

Our estimates of the energy per $p\text{-H}_2$ molecule are in excellent quantitative agreement with those of Ref. 15; on the other hand, we obtain a stronger superfluid signal than they do, especially for clusters with more than ~ 10 molecules. Indeed, we find a robust superfluid signal at the lowest temperature considered here, for clusters comprising as many as $N = 25$ $p\text{-H}_2$ molecules. Analogously to what observed in three-dimensional (3D) clus-

ters, the dependence of the superfluid response on N is non-monotonic.^{10,11}

More importantly, the physical picture that emerges from our study is qualitatively different from that of Ref. 15 in a number of relevant aspects. First and foremost, none of the clusters studied here can be regarded as truly “liquidlike”, at low T . In particular, our radial density profiles for the smaller clusters are quantitatively very different from those of Ref. 15, featuring much higher peaks, separated in turn by much more pronounced dips. This is indicative of a well-defined structure, in which molecules tend to occupy preferred lattice positions, something that is confirmed by our computed density maps. Second, the calculation of the local superfluid density shows that in all superfluid clusters the response is not confined at the surface but rather uniform throughout the system, much like in 3D clusters.¹⁶ Thus, no meaningful distinction can be drawn between a non-superfluid, solidlike center, and a superfluid liquidlike outer part, for any of the superfluid clusters; rather, they should be regarded as featuring concurrently superfluid and solidlike properties. In this sense, these small 2D clusters may be regarded as naturally occurring nanoscale “supersolids”.

The remainder of this article is organized as follows: in the next section we describe the microscopic model underlying the calculation and furnish basic computational details; we devote Sec. III to a thorough illustration of our results, discussing the physical conclusions in Sec. IV, in which we also describe some possible scenarios for the stabilization of a bulk superfluid phase of p -H₂ in 2D.

II. MODEL AND METHODOLOGY

Our system of interest is modeled as a collection of N parahydrogen (p -H₂) molecules, regarded as point particles, moving in two physical dimensions. The quantum mechanical many-body Hamiltonian is the same as in Ref. 15, given by:

$$\hat{H} = -\lambda \sum_{i=1}^N \nabla_i^2 + V(R) \quad (1)$$

where $\lambda = 12.031 \text{ K } \text{\AA}^2$, $R \equiv \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ is a collective coordinate referring to all N particles in the system and $V(R)$ is the total potential energy of the configuration R , which is assumed here to be expressed as the sum of pairwise contributions, each one described by a spherically symmetric potential. In this calculation, we made use of Silvera Goldman potential,¹⁷ mostly for consistency with the calculation¹⁸ of Ref. 15. We computed equilibrium thermodynamic properties of this finite system at low temperature, by means of Quantum Monte

Carlo simulations, based on the Worm Algorithm in the continuous-space path integral representation. Because this methodology is extensively described elsewhere,^{21,22} we do not review it here, but limit ourselves to listing a few important computational details.

Our simulated system is enclosed in a square cell, chosen sufficiently large to remove any effect of the boundary conditions, periodic in all directions. No artificial confining potential was used in the simulation, as clusters stay together simply as a result of the intermolecular pairwise attraction. We use a high-temperature approximation for the imaginary time propagator accurate to fourth order^{23–25} in the imaginary time step τ . The results shown here are obtained with a value of $\tau = 10^{-3} \text{ K}^{-1}$, empirically found to yield estimates indistinguishable, within our quoted statistical uncertainties, from those extrapolated to the $\tau \rightarrow 0$ limit (i.e. the limit where the method becomes exact).

We compute both the global superfluid fraction ρ_S , as well as the radial, angularly averaged one, $\rho_S(r)$. We estimate the first using the well-known “area” estimator,²⁶ the second by means of a straightforward generalization of the area estimator, applied to concentric shells of varying radii, centered at the center of mass of the cluster.²⁷ For the smallest clusters ($N \lesssim 10$), a more accurate estimate of the global superfluid fraction is given by the radial average of $\rho_S(r)$, weighted by the angularly averaged radial p -H₂ density $\rho(r)$, outside of a circle of radius $r_o \sim 2 \text{ \AA}$. This is because the statistical noise in the estimate of ρ_S arises mostly from contributions in the vicinity (i.e., within a distance r_o or less) of the center of mass.

III. RESULTS

As mentioned above, we carried out numerical simulation of clusters at temperatures as low as 0.25 K. In general, structural and energetic properties of the clusters remain essentially unchanged below $T \sim 0.5 \text{ K}$; in particular, physical estimates reported here for $T = 0.33 \text{ K}$ or lower, should be regarded as ground state estimates, within their statistical uncertainties.

Fig. 1 shows the energy per molecule versus cluster size, computed at $T = 0.25 \text{ K}$. Also shown are the results reported in Ref. 15 at a slightly higher temperature ($T = 0.33 \text{ K}$). The two calculations are in excellent agreement, within their statistical uncertainties. The energy per molecule is monotonically decreasing, with no evidence of “magic numbers”, within the precision of our calculation. It attains a value around -15.3 K for a cluster with $N = 30$ p -H₂ molecules; this is still relatively far from the 2D bulk value³ of $\sim -23.2 \text{ K}$.

In order to discuss the structural properties of the clusters, which are the main focus of this study, we begin by illustrating in some details the results for the smallest 2D

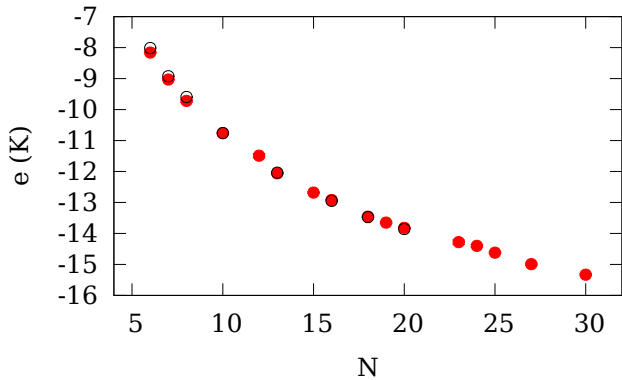


FIG. 1: (color online) Energy per hydrogen molecule e (in K) versus cluster size N , at $T = 0.25$ K (full symbols). Also shown are the results reported in Ref. 15, at $T=0.33$ K (open symbols). For clusters of size $N=13, 16$ and 20 our energy estimates are indistinguishable from those of Ref. 15. Statistical errors are at the most equal to symbol size.

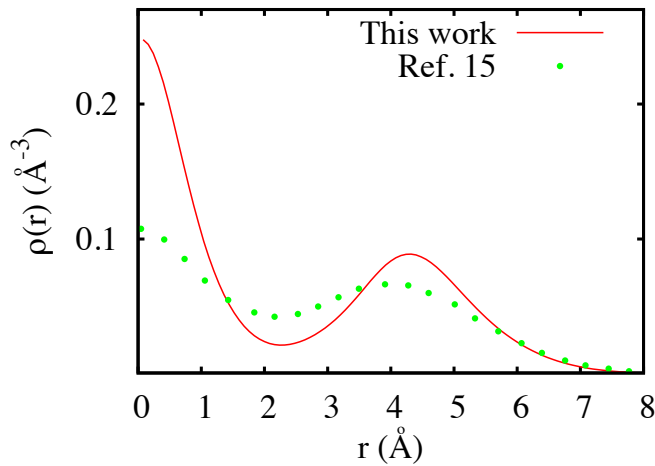


FIG. 2: (color online) Radial density profile for a cluster with $N = 7$ p -H₂ molecules at $T = 0.33$ K (solid line). Filled circles show the corresponding result from Ref. 15. Profiles are computed with respect to the center of mass of the cluster. Statistical errors are not visible on the scale of the figure. The local superfluid density profile for this cluster is indistinguishable from that of the local density.

droplet studied in this work, namely that with $N=7$ p -H₂ molecules, because in many respects this allows us to draw general conclusions, applicable to clusters of greater size as well.

Figure 2 shows the radial density profile $\rho(r)$ for $(p\text{-H}_2)_7$ (solid line), with respect to its center of mass, computed at a temperature $T=0.33$ K. Two results are shown, namely that obtained in this work (solid line), and that published in Ref. 15 (filled circles); for comparison purposes, we begin by discussing the latter first.

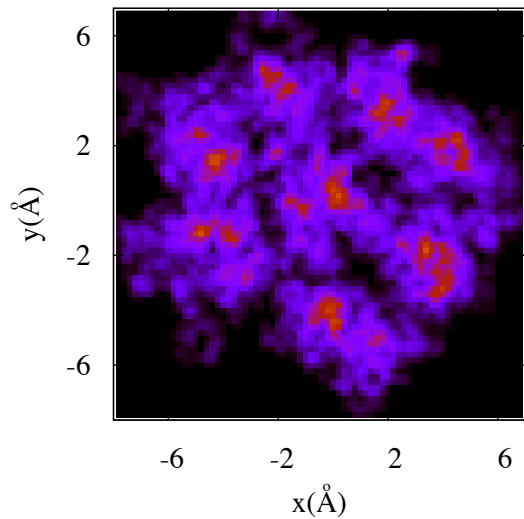


FIG. 3: (color online) Configurational snapshot (particle world lines) yielded by a simulation of a cluster with $N = 7$ p -H₂ molecules at $T = 0.33$ K. Brighter colors correspond to a higher local density.

It displays two broad peaks, one at the origin, signaling a particle in the center of the cluster, and an outer one, ostensibly the signature of a floppy surrounding ring comprising the remaining six molecules. Only a minor depression between the two peaks is observed; indeed, the outer peak is barely detectable. Such a profile was reasonably interpreted by the authors of Ref. 15 as evidence of a structureless, liquidlike cluster.

The corresponding density profile obtained in this work, on the other hand, looks markedly different. It features two much higher and narrower peaks (the one at the origin more than twice as high with respect to that of Ref. 15), separated by a pronounced dip, to suggest a rather sharp physical demarcation between the central particle and the surrounding ring. This points to a considerably more structured cluster, in which particles preferentially tend to be at well-defined relative positions, i.e., the cluster is solidlike.²⁸ The quantitative disagreement between the two results is puzzling, considering that our estimate of the energy per particle ($-8.92(3)$ K), as well as that of the superfluid fraction ρ_S ($\sim 100\%$) at this temperature are in agreement with theirs, within the statistical uncertainties of the calculations. In order to obtain an independent check of our result, we carried out a separate calculation of the ground state properties of this cluster, using the Path Integral Ground State technique.^{25,30} The details of this calculation are identical with those described in Ref. 31. The radial density profile obtained in this second way is identical with that at $T = 0.33$ K, given by the solid line in Fig. 2. This fact gives us confidence on the correctness of our results. The qualitative disagreement with the radial density profile of Ref. 15 is

therefore unclear, as the same microscopic model is utilized.

In order to gain additional insight into the physics of this few-body system, we make use of the direct and visually suggestive information provided in 2D by configurational snapshots generated by the Monte Carlo simulation. (see, for instance, Ref. 29) Fig. 3 shows a particle density map obtained from a statistically representative configuration snapshot (i.e., particle world lines) for the cluster under exam, at the same temperature as in Fig 2. By “statistically” representative, it is meant here that every configuration generated in the simulation is roughly similar to that shown in the figure, differing from it mostly by a mere rotation. Albeit smeared by zero point motion, lumps associated to individual molecules are clearly identifiable, forming an ordered structure, with a visible gap between the particle in middle of the cluster and those in the outer ring. In spite of this relatively “ordered” arrangement, in turn implying a degree of molecular localization, exchanges of indistinguishable particles occur frequently, hence the large superfluid response.

The superfluid fraction of this cluster is, as mentioned above, 100% at $T \leq 0.33$ K, within statistical uncertainty. Moreover, the superfluid signal is uniformly distributed throughout the whole cluster, not concentrated at any specific region (e.g., the surface); in fact, the computed angularly averaged, local superfluid density profile is indistinguishable from that of the local density, shown in Fig. 2. This is much like already observed in 3D clusters.¹⁶ Thus, the two seemingly exclusive superfluid and solidlike properties appear to merge into a single, remarkable “supersolid phase”.²⁸

The same structural short-range order characterizing this small cluster is found in *all* other clusters investigated here. All of them are solidlike, in no case quantum-mechanical exchanges causing the melting at low T into a featureless, liquidlike cluster, an effect which is instead observed in simulations of 3D clusters, in this temperature range.^{10,11} Figures 4 and 5 show radial density profiles for clusters with $N = 13$ and 20 molecules, at $T=0.33$ K. Comparison with Ref. 15 again shows considerably more structure in the simulations carried out here. As the size is increased, both studies yield evidence of greater structural short-range order, but quantitative differences between radial density profiles remain visible even for the largest cluster studied in Ref. 15, i.e., that with $N=20$ (Fig. 5). Our results consistently yield higher peaks and more pronounced dips inbetween, i.e., a significantly more rigid, solidlike structure. This is in marked quantitative, and for the smallest clusters even *qualitative* disagreement with the physical conclusions of Ref. 15.

We now discuss the superfluid properties. For all clusters with $N \leq 22$, the superfluid fraction ρ_s is indistin-

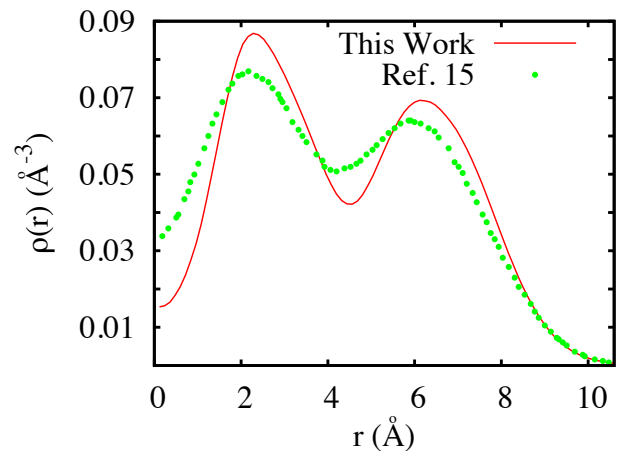


FIG. 4: (color online) Radial density profile for cluster with $N = 13$ at $T = 0.33$ K (solid line). Also shown is the corresponding result from Ref. 15 (filled circles). Profiles are computed with respect to the center of mass of the cluster. Statistical errors are not visible on the scale of the figure.

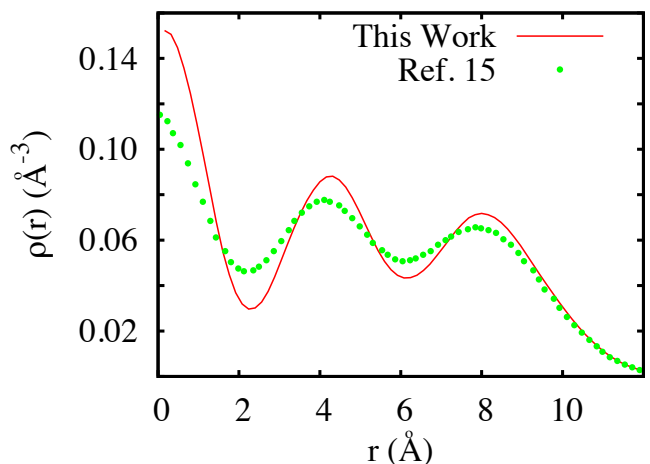


FIG. 5: (color online) Radial density profile for cluster with $N = 20$ at $T = 0.33$ K (solid line). Also shown is the corresponding result from Ref. 15 (filled circles). Profiles are computed with respect to the center of mass of the cluster. Statistical errors are not visible on the scale of the figure.

guishable from 100% within statistical uncertainties at $T = 0.25$ K. Our superfluid signal is stronger than that reported in Ref. 15 for clusters with $N = 13, 16$ and 20, for all of which they find is worth 0.6 ± 0.1 at $T=0.33$ K, whereas for these four specific clusters we find values in excess of 90% at that same temperature. The largest cluster for which a significantly large superfluid response is observed at the lowest temperature considered here, namely $T=0.25$ K, comprises 25 molecules; its superfluid fraction is again worth approximately 100% at $T=0.25$ K.

The superfluid response is observed to drop abruptly for $N > 25$; indeed, for none of the clusters with $26 \leq N \leq 30$ could we obtain an appreciable value of ρ_S in this study,³² at the lowest temperature considered here. It should be noted, however, that the dependence of ρ_S on N for a fixed low T is not monotonic, a fact already observed in 3D clusters^{10,11} with $22 \lesssim N \lesssim 30$. Specifically, at $T=0.25$ K, ρ_S is observed to drop down to level of statistical noise for a cluster with $N=24$, to rebound to $\sim 100\%$ on adding a single molecule (i.e., for a cluster with $N=25$), and to drop again to zero if another molecule is added.

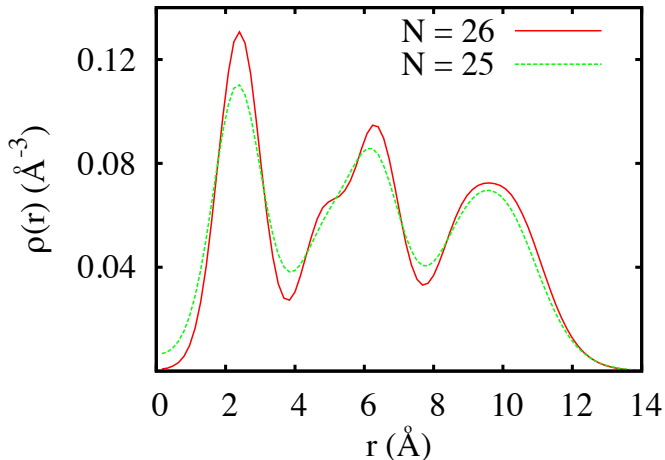


FIG. 6: (color online) Radial density profiles for clusters with $N = 25$ (dashed line) and 26 (solid line) p -H₂ molecules at $T = 0.25$ K. Profiles are computed with respect to the center of mass of the cluster. Statistical errors are not visible on the scale of the figure.

Such an intriguing behaviour, most remarkably mimicking what observed in 3D clusters with the same numbers of molecules, cannot be straightforwardly related to the shape of the cluster, and/or to the completion of any regular geometrical structure, occurring on adding a molecule to (or removing one from) a cluster with $N=25$, nor to some greater “liquidlike” character of the $N = 25$ system. Fig. 6 compares density profiles for the two clusters with $N=25$ and 26 p -H₂ molecules at $T=0.25$, at which the cluster with 25 molecules is entirely superfluid, and that with 26 features no measurable superfluid response. Both profiles show three peaks, i.e., three concentric shells, but that of the cluster with one extra molecule is noticeably more structured, and its first two peaks sharper. On the other hand, the peak corresponding to the outer shell is rather smooth, very similar in both cases. Thus, the main structural difference between the two clusters seems to be that the non-superfluid one has enhanced solid order in the two inner shells. This observation, together with the fact that the superfluid response is uniformly distributed throughout the cluster, in

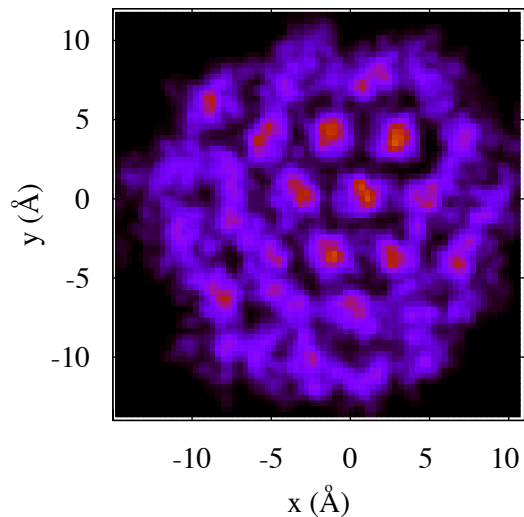


FIG. 7: (color online) Configurational snapshot (particle world lines) yielded by a simulation of a cluster with $N = 25$ p -H₂ molecules at $T = 0.25$ K. Brighter colors correspond to a higher local density.

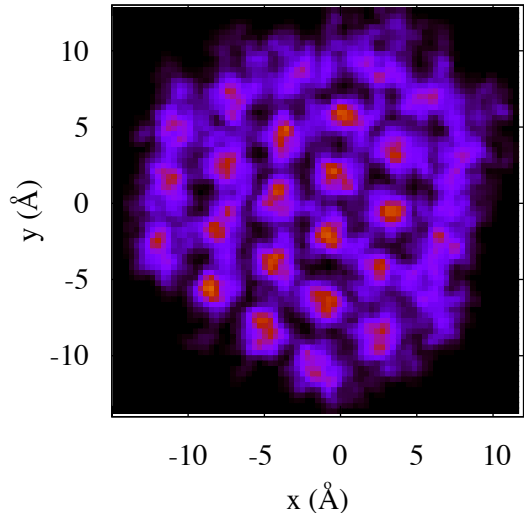


FIG. 8: (color online) Configurational snapshot (particle world lines) yielded by a simulation of a cluster with $N = 26$ p -H₂ molecules at $T = 0.25$ K. Brighter colors correspond to a higher local density.

turn undermines the suggestion that superfluidity should correlate with the presence of a liquidlike outer shell, of which no evidence is shown by the representative configuration snapshots of Figures 7 and 8. Indeed, both clusters display a rather ordered structure, although the molecules sitting at the surface are obviously less bound,

IV. DISCUSSION

We have carried out a systematic investigation of the low temperature properties of small clusters of p -H₂ in two dimensions, using first principle quantum Monte Carlo simulations, whose only input is the intermolecular pair potential. Some of the physical properties of these clusters are very similar to those of clusters in three dimensions. For example, the non-monotonic dependence of the superfluid response at low temperature on the number N of molecules in the cluster, is also observed in the 3D system. There too, most notably, the numbers $N=25$ and 26 are associated with the same effect observed here, i.e., the drop of the superfluid fraction from nearly 100% to a value close to zero (in the temperature range considered here), on adding a single molecule to the $N=25$ cluster. This suggests that a remarkable compensating effect takes place on reducing dimensionality; the enhancement of quantum fluctuations, and the concomitant suppression of quantum-mechanical exchanges (due to the confinement of molecular motion to a plane, and the hard, repulsive core of the intermolecular potential at short distances) both contribute to preserve some of the same physics observed in three dimensions.

On the other hand, some of the features of 2D p -H₂ droplets set them aside from their 3D counterpart. The most striking feature of these few-body systems, is the simultaneous presence of what can be reasonably described as short-range order, whereby molecules tend to form specific geometrical arrangements, typically resulting from a classical mechanism (i.e., minimization of potential energy), and a finite superfluid response, originating from exchanges of identical molecules. Much like in the 3D case, superfluidity is underlain by cycles of exchanges involving all of the molecules, not just those on the outer shell. Indeed, the participation of inner molecules to exchanges is crucial, witness the fact that as the number N is increased beyond 25, at which point the superfluid response of the clusters is significantly suppressed, their inner structure concurrently appears much more rigid (as shown by the comparison in Fig. 6), consistently with inner molecules to be more localized and

less involved in exchanges.

What are the implications of this study, if any, regarding a possible stabilization of a superfluid phase of bulk p -H₂? The suggestion that one might be able to use frustration, either arising from disorder^{7,33} or from an underlying impurity substrate incommensurate with the equilibrium triangular crystalline phase of p -H₂ in two dimension,⁵ has not been shown to lead to a superfluid phase, although recently renewed claims to that effect have been made.³⁴

An alternative approach could borrow on ideas arising from theoretical studies of superfluidity (and supersolidity) in cold atom assemblies.³⁵ Specifically, one could imagine patterning a suitably chosen surface with regularly arranged adsorption sites (e.g., on a triangular lattice). Each site could be designed to accommodate a number of p -H₂ molecules between, say, ten and twenty, acting in a sense as a “molecular quantum dot”, turning superfluid at low T . Conceivably, upon choosing the lattice constant of the adsorption lattice suitably, it might be possible to establish phase coherence throughout the whole system, through the tunnelling of individual p -H₂ molecules across adjacent adsorption wells. The ensuing superfluid phase would be similar to the supersolid droplet crystal phase of Refs. 36 and 37, with the important conceptual difference that in the present case the adsorption lattice is externally imposed, as opposed to arising from inter-particle interactions. This scenario is presently being investigated by computer simulation.

Acknowledgments

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